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Magnetic structures and magnetic phase transitions in RMn$_2$Si$_2$

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Magnetic properties of the $LaMn_2Si_2$ and $La_{0.6}R_{0.4}Mn_2Si_2$ (R = Sm, Tb, Gd) compounds with layered $ThCr_2Si_2$-type structure have been studied using quasi-single-crystalline and polycrystalline samples. Substitution of the R atoms for La decreases the interatomic distances and changes the ordering of the Mn sublattice from ferromagnetic to antiferromagnetic. Magnetic structure of the substituted compounds has been found to depend on the anisotropy of R ions. The Sm moments are oriented in the basal plane and weakly coupled with the Mn sublattice. For R = Tb, frustrations prevent the formation of long-range magnetic ordering in Tb sublattice. For the system with Gd, the antiferromagnetic Mn-Mn and Gd-Mn interactions lead to a change of magnetic anisotropy from the easy-axis to the easy-plane type.
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I. INTRODUCTION

Intermetallic compounds RMn$_2X_2$ (R is a rare earth element, X is Si or Ge) crystallize in a body-centered tetragonal $ThCr_2Si_2$-type structure (space group $I4/mmm$). In this structure, the R, Mn and X atoms form separate layers stacked along the c-axis in the sequence -Mn-X-R-X-Mn-.[1] The compounds are of considerable attention since they demonstrate a variety of magnetic structures and magnetic phase transitions.[1–4] At low temperature the Mn magnetic moments possess either collinear or canted ferromagnetic ordering within each Mn layer, while the average magnetic moments of adjacent Mn layers can be oriented either parallel or antiparallel to each other, thus forming ferromagnetic (F) or antiferromagnetic (AF) structures.[5,6] At elevated temperatures, a collinear in-plane antiferromagnetic structure is observed for some compositions. At low temperatures, rare-earth atoms with nonzero magnetic moment can develop low-temperature ferromagnetic ordering which influences the structure of the Mn sublattice due to the R-Mn exchange interaction.

Numerous systematic studies of different ternary and quasi-ternary RMn$_2X_2$ compounds have shown that the exchange interactions between adjacent Mn layers strongly depend on the in-plane Mn–Mn distance, $d_{\text{Mn-Mn}}$, and consequently, on the lattice constant $a = \sqrt{2}d_{\text{Mn - Mn}}$.[1,2,7] For the compounds in which $d_{\text{Mn-Mn}} > d_c \approx 0.285 - 0.287$ nm, the intralayer in-plane alignment is antiferromagnetic and the interlayer coupling is ferromagnetic. When $d_{\text{Mn-Mn}}$ value is below d_c but larger than 0.284 nm, both the intralayer and interlayer couplings are antiferromagnetic. If the distance $d_{\text{Mn-Mn}}$ is smaller than 0.284 nm, there is no intralayer in-plane spin component and the interlayer coupling remains antiferromagnetic. For ternary RMn$_2$Si$_2$ compounds, the condition $d_{\text{Mn-Mn}} > d_c$ is satisfied for R = La. At room temperature the lattice constants of the $LaMn_2Si_2$ are a = 0.4114 nm, c = 1.0617 nm, and the shortest in-plane Mn-Mn distance amounts to 0.2909 nm.[8] Accordingly, $LaMn_2Si_2$ is a ferromagnet below T_C = 305 K. The RMn$_2$Si$_2$ compounds with other R elements have smaller lattice constants, and the in-plane Mn-Mn distance lies below the d_c value.

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For a particular case when the Mn-Mn intralayer distance is close to d_c, the AF-F magnetic phase transition can be induced by temperature (as a result of the lattice thermal expansion) or by application of a moderate magnetic field. The condition $d_{\text{Mn-Mn}} \approx d_c$ can be obtained in the quasi-ternary $La_{1-x}R_xMn_2X_2$[9,10] compounds where the interatomic distances can be finely tuned by changing the composition. A variety of magnetic phase transitions makes these systems attractive for magnetostriction[11] and magnetocaloric studies.[12,13]

In the present paper, in order to reveal the contribution of rare-earth sublattice to the magnetic state and magnetic phase transitions in RMn_2Si_2 with antiferromagnetic interlayer Mn-Mn coupling, we studied magnetic properties of several $La_{1-x}R_xMn_2Si_2$ (R = Sm, Tb and Gd) compounds for which the in-plane Mn-Mn distance is below its critical value d_c. It is expected that an increase in x leads to an increase in the R–Mn exchange interactions in all the systems. The Gd ion possesses zero orbital momentum and its contribution to the magnetocrystalline anisotropy should be very small. Both the Sm and Tb contribute to the magnetic anisotropy. The electron f shell of the Sm and Tb ions is characterized by the Stevens factor of opposite signs, which can provide various orientations of magnetic moments of the R ions.

II. EXPERIMENTAL DETAILS

The alloys were prepared by induction melting of the constituents in an argon atmosphere followed by annealing at 900°C for one week. The phase composition was controlled by powder X-ray diffraction analysis performed with the DRON-6 diffractometer in Cr K_α radiation. All the compounds were found to crystallize with $ThCr_2Si_2$-type structure; the amount of additional phases does not exceed 3 %.

For the magnetization studies, the $La_{1-x}Sm_xMn_2Si_2$ powders were aligned at room temperature in an external magnetic field up to 15 kOe and fixed by an epoxy resin. It was confirmed by X-ray diffraction analysis that the alignment direction corresponds to the crystallographic c-axis. For the systems with Tb and Gd, by checking large grains of the ingot we succeeded to select quasi-single crystal samples in the form of plates. X-ray back-scattered Laue analysis confirmed that the plates consist of several crystallites, the tetragonal c-axes of which are oriented strictly perpendicular to the plate plane, while the a-axes of crystallites are partially disoriented within the plane of the plate.

The magnetization measurements were performed with Quantum Design MPMS5 XL SQUID magnetometer in magnetic fields up to 50 kOe. High-field magnetization curves were measured by an induction method in pulsed magnetic fields up to 300 kOe with a pulse duration time of ~ 10 ms.

III. RESULTS AND DISCUSSION

Since lanthanum is a non-magnetic 4f-element, magnetic properties of $LaMn_2Si_2$ are mainly due to the Mn sublattice. According to neutron diffraction studies,[3] at low temperature the Mn magnetic moments deviate by the angle 46° with respect to the c-axis, and the interlayer ordering is ferromagnetic, as it tentatively shown in the inset in Fig. 1. The magnetization curves of $LaMn_2Si_2$ measured in magnetic fields parallel and perpendicular to the c-axis (Fig. 1) are typical for a uniaxial ferromagnet. Almost linear $M(H)$ dependence for $H \perp c$ is indicative of a small misalignment angle (~4°) of the easy axes of separate crystallites. Along the alignment direction, the magnetization saturates in the field above 15 kOe. Since the high-field magnetic susceptibility is low, deformation of non-collinear magnetic structure in the applied magnetic fields up to 50 kOe is relatively small. For the hard direction, the saturation is expected at the anisotropy field of ~ 60 kOe. The anisotropy constant is estimated as $K_1 = 6.5\times10^6$ erg/cm^3[8] that is rather high value for the 3d-metal sublattice.

Our X-ray diffraction data confirmed that for all studied $La_{1-x}R_xMn_2Si_2$ compounds the in-plane Mn-Mn distance decreases with increasing x and passes through the critical value d_c = 0.287 nm. For R = Tb and Gd the critical concentration is x_c = 0.27,[7] while in the system with Sm the critical concentration is close to 0.4 at room temperature.[10] Therefore, for our comparative study we selected the $La_{0.6}R_{0.4}Mn_2Si_2$ compositions.

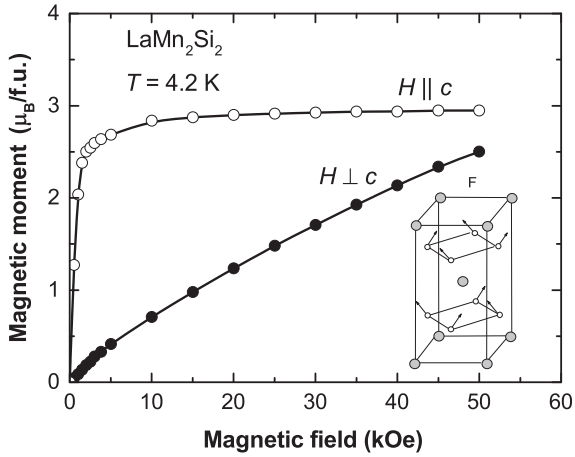

FIG. 1. Magnetization curves of $LaMn_2Si_2$ measured along (open symbols) and perpendicular (closed symbols) to the *c*-axis. Inset shows schematically the orientations of the Mn magnetic moments refined in Ref. 3.

Figure 2 shows magnetization curves of $La_{0.6}Sm_{0.4}Mn_2Si_2$ measured in high pulsed magnetic field at 77 K. It is seen that the compound has no spontaneous magnetization. Independently of the applied field direction, the compound exhibits a field-induced AF-F transition. The transition field value is lower for the field applied along the *c*-axis. Our detailed studies of the $La_{0.75}Sm_{0.25}Mn_2Si_2$ single crystal showed that magnetic ordering of Sm sublattice appears below 14 K.[14] The Sm moments are oriented in the basal plane, and the Sm-Mn exchange interaction is very weak even at 2 K.[10,14]

In the system with terbium, the low-temperature magnetic ordering is different from that with Sm. The Tb sublattice possesses a strong axial magnetic anisotropy.[7] At low temperature the inter-sublattice Tb-Mn exchange interaction in $TbMn_2Si_2$ is large enough to break negative Mn-Mn interlayer coupling. As a result, a collinear ferrimagnetic structure is formed.[15] In the quasi-ternary $La_{1-x}Tb_xMn_2Si_2$ the exchange interaction between the rare-earth and Mn layers gradually changes with *x*.

Figure 3 shows field dependences of magnetic moment of $La_{0.6}Tb_{0.4}Mn_2Si_2$, measured along the easy *c*-axis and in the basal plane at 4 K. The magnetization curves show neither hysteresis nor spontaneous magnetization, which points to the paramagnetic or antiferromagnetic ground state. For the case of AF ordering of both the Tb and Mn sublattices with the easy *c*-axis, one

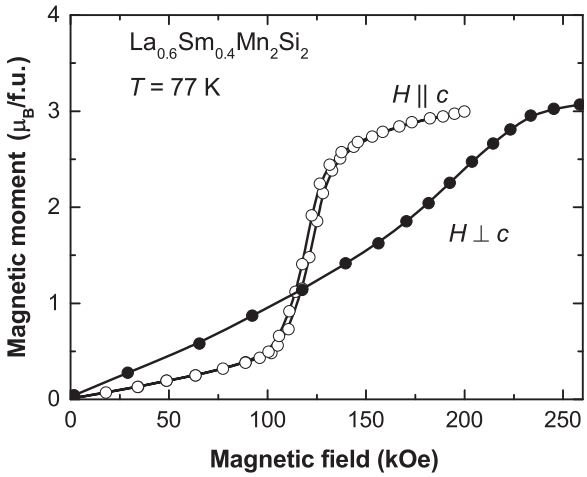

FIG. 2. Magnetization curves of $La_{0.6}Sm_{0.4}Mn_2Si_2$ measured along (open symbols) and perpendicular (closed symbols) to the *c*-axis.

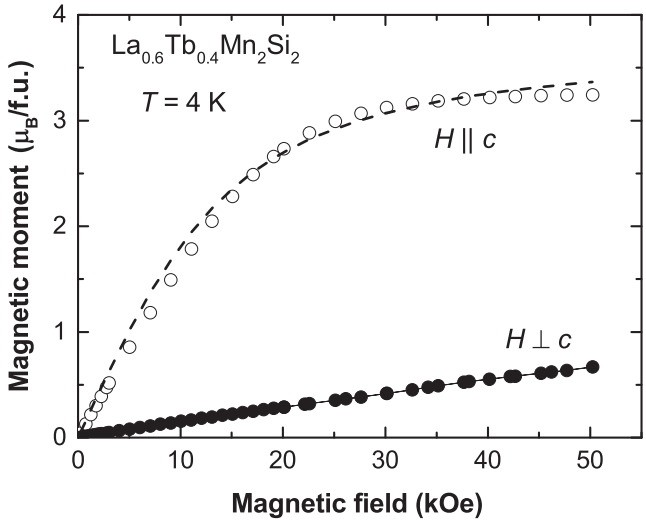

FIG. 3. Magnetization curves of $La_{0.6}Tb_{0.4}Mn_2Si_2$ measured along the *c*-axis (open symbols) and in the basal plane (closed symbols) at 4 K. Dashed line shows magnetization calculated with Brillouin function.

can expect a very small initial magnetic susceptibility in magnetic fields applied along the *c*-axis. As seen from Fig. 3, experimental susceptibility value is higher for the *c*-axis than in the basal plane.

An alternative model assumes antiferromagnetic ordering of the Mn sublattice and paramagnetic state of the Tb moments. Field dependence of magnetization *M* for the paramagnetic Tb sublattice can be described by the Brillouin function:

$$M(H,T) = xg_J J \cdot B_J\left(\frac{g_J J \mu_B H}{k_B T}\right). \quad (1)$$

Here *x* is the Tb concentration, $g_J = 3/2$ is the Landé factor, $J = 6$ is the total quantum number for Tb^{3+} ion, μ_B is the Bohr magneton, k_B is the Boltzmann constant. The $M(H)$ dependence calculated using (1) with no fitting parameters is shown by dashed line in Fig. 3. It is seen that the model of paramagnetic Tb sublattice gives good explanation of the observed magnetization curve of $La_{0.6}Tb_{0.4}Mn_2Si_2$ along the *c*-axis at 4 K. We assume that the Tb atoms are in a frustrated state with respect to the Tb-Mn interplane interactions. On contrary to $TbMn_2Si_2$, in $La_{0.6}Tb_{0.4}Mn_2Si_2$ the in-plane Tb-Tb indirect exchange is probably too small to order magnetic moments within the Tb layers, and the Tb-Mn exchange interaction is too small to break negative Mn-Mn interlayer coupling. A competition of the interlayer Mn-Mn and Tb-Mn exchange interactions and strong uniaxial magnetic anisotropy of both the Tb and Mn sublattices lead to formation of frustrated magnetic state of the Tb moments, which prevents the long-range magnetic ordering in the Tb sublattice. Our neutron diffraction data[16] are consistent with these findings.

On contrary to the compound with Tb, the magnetization curves of $La_{0.6}Gd_{0.4}Mn_2Si_2$ compound show ferromagnetic behavior (Fig. 4) with rather high magnetic anisotropy. The anisotropy field is estimated as ~ 100 kOe. Since Gd ions have zero orbital momentum, the magnetic anisotropy should be due to the Mn sublattice. However, as shown in Fig. 1, the Mn provides a uniaxial magnetic anisotropy in $LaMn_2Si_2$, whereas for $La_{0.6}Gd_{0.4}Mn_2Si_2$ the easy magnetization direction lies in the basal plane. Therefore, upon partial substitution of Gd for Tb, for the low-temperature region, the change in the type of the interlayer Mn-Mn ordering from ferromagnetic to antiferromagnetic is accompanied by a spin-reorientation transition from the easy *c*-axis to the basal plane. The combination of negative Gd-Mn and Mn-Mn interlayer exchange interactions and the easy-axis type magnetocrystalline anisotropy of the manganese sublattice leads to appearance of an unexpected non-collinear magnetic structure in which the resulting magnetic moment is oriented perpendicular to the direction of the easy *c*-axis of the Mn sublattice.

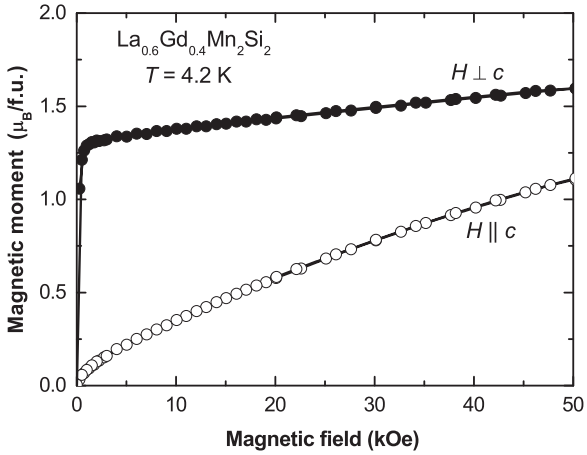

FIG. 4. Magnetization curves of $La_{0.6}Gd_{0.4}Mn_2Si_2$ measured along the *c*-axis (open symbols) and in the basal plane (closed symbols) at 4.2 K.

IV. CONCLUSION

In order to determine contribution of magnetic rare-earth sublattice to the formation of magnetic structures and magnetic phase transitions in RMn_2Si_2 compounds with layered $ThCr_2Si_2$-type structure, we studied magnetic properties of the $LaMn_2Si_2$ and $La_{0.6}R_{0.4}Mn_2Si_2$ (R = Sm, Tb, Gd) using quasi-single-crystalline and aligned polycrystalline samples. For these compounds, the type of the interlayer Mn-Mn magnetic ordering depends on the intralayer Mn-Mn distance. $LaMn_2Si_2$ is a uniaxial ferromagnet with a relatively high anisotropy constant $K_1 = 6.5\times10^6$ erg/cm^3 at 4.2 K. Substitution of the R atoms for La leads to a decrease of the interatomic Mn-Mn distance, and the interlayer ordering of the Mn sublattice in $La_{0.6}R_{0.4}Mn_2Si_2$ is antiferromagnetic. Since magnetic R atoms in the lattice are located in between two antiferromagnetically coupled Mn layers, a frustrated magnetic state appears with respect to the negative R-Mn interactions. Because of the frustrations, the Tb sublattice in $La_{0.6}Tb_{0.4}Mn_2Si_2$ remains paramagnetic down to 4 K, while Gd and Mn in $La_{0.6}Gd_{0.4}Mn_2Si_2$ form a non-collinear magnetic structure in which the total magnetic moment is oriented in the basal plane.

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